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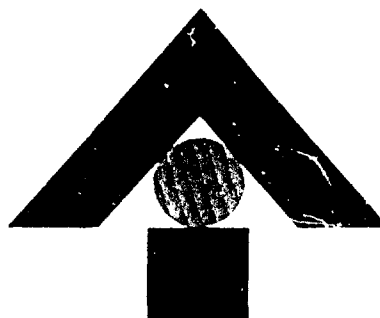
Report 63-136

**AN ACCIDENTAL EXPLOSION  
INVOLVING THE USE OF OXYGEN  
DIFLUORIDE**

Contract AF33(657)-9162  
Project No. 62-2899-7381, Task No. 783103  
November 1963

**ASTROPOWER, INC.**

SUBSIDIARY OF THE DOUGLAS AIRCRAFT COMPANY, INC.



2121 PAULARINO AVENUE NEWPORT BEACH, CALIFORNIA

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Administered By  
Applications Division  
Air Force Materials Laboratory  
Research and Technology Division  
Air Force Systems Command

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## FOREWORD

This report was prepared by Astropower, Inc. under Air Force Contract AF33(657)-9162, Project 7381, Task 783103. The work was administered by the Applications Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, with Mr. W. P. Conrardy as Project Engineer.

This report describes an accidental explosion involving the use of oxygen difluoride which occurred during testing under the subject contract and resulted in destruction of the long-term immersion tests and severe injury to the attending technician. The conditions leading to the explosion are analyzed, and the results of preliminary investigation of the conditions that prevailed at the time of explosion are described. Although specific cause of explosion remains unknown certain suggestions are made to minimize some potential hazards associated with the use of this oxidizer.

Astropower's work on the project was conducted under the direction of Dr. N. A. Tiner, Head of the Materials Laboratory, with Dr. W. D. English as the principal contributing scientist. Mr. R. Williams was the research technician injured while attending the long-term immersion tests.

Messrs. S. W. Pohl, W. G. Black, D. V. Moberg, and W. A. Cannon of the Materials Laboratory, Mr. R. S. Pickford, Head of the Mechanical and Ordnance Engineering Department, and Mr. C. D. Milner, Jr. of the Safety Department have given able technical assistance in the investigation and preparation of this report. Their valuable contributions are acknowledged with gratitude.

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## 1.0 INTRODUCTION

Oxygen difluoride ( $\text{OF}_2$ ) is a very powerful oxidizing and fluorinating agent. It has a number of characteristics which give it distinct advantages over oxygen and fluorine, and it also provides good specific impulse performance with both carbon- and non-carbon-type rocket fuels. In addition to their high performance characteristics,  $\text{OF}_2$  systems are hypergolic.

Oxygen difluoride is stable at room temperature, and its stability increases as the temperature is lowered. Most of the known metallic elements react with it only upon heating to the range of 300-500°C. At lower temperatures it is reported to be inert with carbon, rubber, plastics, glass, and common metals. However, some accidental explosive reactions of unknown nature have been reported, and Sidgwick<sup>(1)</sup> states that if the gas is at too high a pressure when it is brought into contact with charcoal, violent explosions may occur.

A number of engine development programs for space applications have been conducted with oxygen difluoride. It is space-storable and can be pressurized under its own vapor pressure, or equilibrium temperatures can be established in a space vehicle below the boiling point (-144.8°C) and within the absorptivity/emissivity ratios.

The general corrosion behavior of this oxidizer has been considered in the literature, but quantitative information on specific compatibility with engineering structural materials is very limited. In order to fill this gap and to provide additional data for evaluation of the feasibility of using  $\text{OF}_2$  in various space applications, Astropower is conducting a fairly extensive corrosion program under Air Force Contract AF33(657)-9162. The program is sponsored by the Air Force Materials Laboratory, with Mr. W. P. Conrardy as Project Engineer.

One phase of this program consists of immersion of structural materials in gaseous and liquid  $\text{OF}_2$  for short periods of one and 21 days, and for longer periods of four and 12 months at -109°F at a saturation pressure of 500 psi. These tests are being conducted at Astropower's Gypsum Canyon Test Range. The test procedures and the results of short-term tests have been thoroughly described in progress reports on the contract.<sup>(2)</sup>

On 15 October 1963, during maintenance of the immersion baths of the long-term test containers, an explosive reaction or deflagration occurred. It was confined to one test bay only, but resulted in the destruction of the long-term immersion test setup and severe injury of the research technician attending to the immersion bath in the test bay. This report describes the nature of this accidental explosion and the results of preliminary investigation made. Some potential hazards associated with the use of oxygen difluoride are pointed out, and recommendations are made to eliminate them.

## 2.0 GENERAL DESCRIPTION OF TEST PROCEDURES

A general view of the fluorine test facility and the test bay where immersion tests are conducted for long time periods are shown in Figures 1 and 2. The test setup and the flow system are schematically illustrated in Figures 3 and 4.

Manipulation of oxygen difluoride is highly dangerous due to its reactivity and toxicity, and all operations involving flow of this oxidizer are carried out from behind a concrete wall. Main cylinder valves are operated from the control room by a chain-and-sprocket arrangement. All other manifold valves are manipulated by means of handles which pass through the concrete wall of the control room. All the inlet and outlet valves connecting inert gases ( $\text{GN}_2$ ,  $\text{GHe}$ , and vacuum supply) and the oxidizer transfer lines to the test bombs are operated from the safe side of the 6 ft high concrete wall of the test bay (Figure 3).

Several steps comprise the procedure for carrying out corrosion tests. All specimens and apparatus to be used in the test are cleaned to "LOX-clean" standards in a "clean room." New metal parts which have not been previously used are passivated in nitric acid, cleaned, passivated with gaseous fluorine, and then recleaned (this passivation is not applied to test specimens). The cleaned specimens are loaded into Teflon racks. The racks are inserted in test bombs, tops are installed, all fittings are attached, and openings are sealed tightly (see Figure 5). It may be noted that overpressure relief devices are not included in the construction of the sample containers, which are a type of compressed gas cylinder, following the recommendation of the AEC.<sup>(3)</sup> The assembled apparatus is transported to the test bay and placed in the support assembly, and three test bombs are attached to one common tubing manifold. This constitutes a test bomb array (see Figure 4).

The test bombs and attached fittings and lines are tested for leaks with  $\text{GN}_2$  at 600 psi. The pressure is released, the connection to the high pressure  $\text{GN}_2$  supply is sealed off, the valves to the main manifold are opened, and the entire system is evacuated for several hours, then checked for vacuum leaks. Meanwhile, a Dewar flask is raised around the bomb array and filled with  $\text{LN}_2$ . When thermal equilibrium is reached, the vacuum pump is isolated, and the flow of oxidizer is opened into the evacuated manifold. After the required

quantity of oxidizer is condensed in each bomb, the supply is turned off, the bomb inlet valve is closed, the manifold is flushed with  $\text{GN}_2$ , the supply lines are disconnected, and the fittings are sealed with pressure caps. The Dewar containing  $\text{LN}_2$  is rapidly lowered with an air-operated jack, and an insulated bath charged with Freon MF (fluorotrichloromethane-carbon tetrachloride) and Dry Ice is substituted and raised around the test bomb array to the position shown in Figure 4. An insulated cap of foamed glass is placed over the top opening of the bath.

The Dry Ice in the bath must be replenished periodically to keep the temperature constant at  $-109^\circ\text{F}$ . At least once daily the gauge pressure readings are recorded, the glass foam insulator is removed from the top of the bath (see Figure 3), crushed Dry Ice is placed in the bath, and the top is covered.

At the end of the selected time interval (21 days, four months, etc.), the exit valve from the bomb array is opened slightly, and the oxidizer is allowed to flow out through the exhaust system and is vented through a charcoal-containing scrubber. When the pressure has decreased to 100 psi, the cooling bath is lowered, and all oxidizer is allowed to escape. The array is then flushed with  $\text{GN}_2$  and evacuated several times, the supply lines are reattached, and the array is purged with  $\text{GN}_2$  for several hours. Finally, the test bombs are detached from the manifold and all openings are sealed. The containers are transported to another area, where they are opened and the specimens are removed and examined.

These operations have been successfully conducted on a regular basis during the past year, and more than 12 test bomb arrays have been immersion tested with oxygen difluoride and 12 with a mixture of dinitrogen tetrafluoride ( $\text{N}_2\text{F}_4$ )-perchloryl fluoride ( $\text{FClO}_3$ ). The accidental explosion which resulted in the destruction of the immersion test setup and severe personal injury occurred when the research technician was replenishing the constant temperature bath with crushed Dry Ice.

### 3.0 DESCRIPTION OF EXPLOSION

Four long-term exposure tests were in progress in the test bay on the day of the accident. Two of them were tests involving oxygen difluoride (FO-10 and FO-17), and two involved a mixture of 50% perchloryl fluoride-50% tetrafluorohydrazine (Tests PNF-10 and PNF-13). The physical arrangement of the tests is shown schematically in Figure 3.

The main supply valve connecting the tubing manifold in the test bay to the supply manifold was known to be closed, since this setting had been checked prior to leak testing the new test scheduled to begin in the next test bay. The exit valves from all tests were closed, as no pressure drops due to loss of oxidizer through the vent line had occurred. Pressures in all the tests were in the normal range, as shown by readings which had been recorded as a standard operating procedure immediately prior to servicing the cooling baths with Dry Ice. The FO-17 test bomb array had 505 psi recorded pressure.

The technician was replenishing the bath around test FO-17 with Dry Ice when the explosion occurred. The Project Scientist was about 12 ft away from the test setup and on the other side of the concrete wall. Icing of Tests PNF-13 and FO-10 had been completed, and the technician was standing on a roll-around ladder while gently tamping crushed Dry Ice into place in Test FO-17 with a wooden stick. The Project Scientist observed about 2 min before the explosion that the icing procedure was being conducted in a routine manner.

The technician later reported that he felt a tremendous blow and a sensation like a strong electric shock. The ladder was blown from under him, and he was knocked down to the floor of the bay. His boots, shirts, and part of his trousers pants were blown off, and both legs and one arm received severe injuries. He was taken to hospital in critical condition.

There were two distinct explosions approximately 1/10 sec apart. This was heard by persons away from the test facility; the technician and the Project Scientist did not perceive two separate blasts. A violent physical jolt and a flash of light accompanied the detonations. It was reported that, looking toward the building, there were observed some roof panels flying through the air, two separate plumes of brown smoke which rapidly turned to white, and a rain of red-hot or flaming objects. All outdoor portions of the test facility

were enveloped in a cloud of dense, white, unbreathable fumes. The fumes were a combination of pungent  $\text{OF}_2$ , HF, and other components which took several minutes to dissipate.

After rescue of the injured technician, an immediate check of the facility was made. There were no signs of fire inside the facility. Both FO-17 and FO-10 exposure tests had been destroyed, and the test bombs and test coupons were strewn over a wide area. The Bourdon tubes on test gauges had burst, tubing lines had broken away or bent, and the support frame was bent and broken. The two PNF-10 and PNF-13 tests had been heavily shocked, twisted out of position, and their cooling baths partially dumped. Several aluminum panels were ripped off the roof, and puncture holes were seen in the remaining roof panels. The south wall of the test bay was cracked and displaced. The insulated baths from the tests were ripped to shreds, and pieces of foamed glass and polyurethane lay throughout the area (see Figures 6 and 7). A small brush fire started outside 300 ft from the test bay and was quickly extinguished.

After inspection by the Air Force and insurance agencies was completed, a thorough cleanup and search of the facility and surroundings was carried out. All test coupons, bomb parts, and other associated materials were collected, tagged, and their location marked. An investigation of the cause of explosion was initiated.

#### 4.0 OBSERVATIONS ON THE MECHANISM OF EXPLOSION

##### 4.1 Test Apparatus

Test FO-17 was the source of the initial explosion. This was followed within an estimated 1/10 sec by explosion of Test FO-10.

Several pieces of evidence support this sequence. The technician was conscious and stated he was servicing Test FO-17, and only personnel 500-1000 yd away from the facility reported two distinct explosions. The jacket of the insulated bath for Test FO-10 was wrapped firmly around the vertical steel support rod adjacent to Test FO-17. In addition, the debris from Test FO-10 was found on the floor on top of debris from FO-17, indicating that the latter test exploded first. The distinct imprint of the base of one bomb on the bottom of the jacket of the insulated bath indicates that one bomb exploded and drove through the container in such a manner as to preclude any subsequent direct impact between the other two bombs in the array.

The possibility of shock wave or detonation propagation through 1/8 in. tubing connecting the test bombs appears unlikely, as evidenced in the appearance of connecting tubes and the manner in which they were plumbed. It is extremely difficult to propagate a shock or detonation wave through such small diameter tubing because of the pronounced boundary layer effects and large heat waves to the tubing wall. In only one instance did a piece of tubing show a "banana peel" failure, indicating the passage of a shock or detonation. In this case, heat discoloration in the fracture area indicated either a detonation or the presence of hot combustion gases forced into the tube from the bursting bomb (see Figure 8).

Several pieces of tubing were blown out of Swagelock fittings. The Bourdon tubes on both FO-10 and FO-17 test gauges were burst. Tubing lines broke away from flare fittings at the end of the sleeves; flares did not pull out. Some tubing lines were bent double and broken at the bends. (These lines ran through the blast area but were not connected to the OF<sub>2</sub> tests.)

Propagation of pressure waves between the two tests via 1/8 in. tubing to initiate the second explosion can also be ruled out because of the length of lines involved and the presence of connecting valves, which were in



a closed position. The mechanism of the valve connected to Test FO-17 was jammed, and the valve showed a very slight leak port-to-port. The bellows had no leak. The valve connected to Test FO-10 showed a burn mark on the face of the plug opposite the opening from the port to which the test was attached. It had an appreciable leak rate port-to-port when closed (1000 cc of  $\text{GN}_2$ /min at 500 psi). The bellows were undamaged.

The appearance of the six test bombs and bomb lids is shown in Figures 9 and 10. The bombs were not distorted appreciably, but the lids were cupped 0.010 to 0.020 in. Lid No. 1 was distorted 0.090-0.095 in. on the arc. The bolts were tension sheared and strewn over a wide area. All three bombs from Test FO-17 showed severe erosion in the area of the gasket sealing surfaces between the main body and the lid. Erosion was also noted on the bolt flange. Only one bomb (No. 1) from Test FO-10 showed any erosion. The lid from bomb No. 3 showed rapid separation with slight erosion.

The erosion of the bombs was associated with the outrush of gaseous  $\text{OF}_2$  at high temperature. It is inferred that the pressure inside the bomb increased rapidly due to some exothermic reaction. The observations previously made with uncooled flame deflectors by Mr. Pickford<sup>(4)</sup> appear to indicate that the type of erosion in such a short duration, as noted above, would indicate temperatures well in excess of 6000°F. The heat transfer coefficient for expanding gases in general shows a marked increase at Mach 1, and the kinetic forces exerted against the metal surface have a marked peak in the range of Mach 1 to 1.5. This range of sonic flow would take place near the gasket surfaces and both flanges, causing erosion to occur in these areas.

#### 4.2 Test Specimens

An evaluation was made of the scattering of test specimens and bomb parts, and of the appearance of specimens recovered, in order to clarify the manner in which the explosion occurred and determine its intensity (see Figures 11 and 12, and Tables I and II). Lid No. 5 of Test FO-17 was found 7 ft east of the bay; the other two lids were blown out through the roof to a considerable distance from the facility and could not be found. Lid No. 3 of Test FO-10 was found on the roof, and lids No. 1 and No. 7 were in the bay.

The test specimens from bomb No. 5 (Test FO-17), which were basically Al alloy and Teflon, were found 10% in the bay and 90% scattered in the wind direction (see Figure 11). The Teflon showed reaction and considerable deterioration. Some Al-5456 and Al-6061 specimens showed considerable distortion of a mechanical nature; other specimens from the same alloys (D, F) were reasonably straight (Figure 13).

The test specimens from bomb No. 8 (Test FO-17), which were basically stainless steel, were recovered 31% in the bay and 69% at nearby locations. The specimens were reasonably unaffected, except those of stainless steel Type 316 (J), which showed mechanical distortion. The test specimens from bomb No. 13 (Test FO-17) were recovered 17% in the bay and 83% at considerable distances, the majority being found on the roof. The nickel-base alloy specimens did not show any damage. Titanium alloy Al10AT (T) exhibited self-sustained burning on the edges. Columbium and tantalum were badly distorted and exhibited excessive heating on the edge surfaces (Y, AA). Of the four specimens of graphite A, G, K, S, P, only three small pieces were recovered in the bay. They crumbled easily under pressure, as compared to the "as-received" specimens. X-ray diffraction analysis of the basal (0002) planes of "as-received" material had a  $2\theta$  angle of 26.30 radians ( $3.386 \text{ \AA}$ ), and immersion test material had a  $2\theta$  angle of 26.40-26.42 radians ( $3.371\text{-}3.369 \text{ \AA}$ ). The slight contraction of the d-spacings noted might be attributed to the formation of fluoride bonds in the basal planes.

The scattering of specimens from Test FO-10 is shown in Figure 12, and the appearance of test specimens from three bombs in Figures 16 to 18. The scattering of aluminum alloy samples from bomb No. 3 was very extensive. Al-1100 samples showed excessive mechanical damage, particularly in the gas phase. This bomb also contained columbium samples (Y) which exhibited severe distortion and heating on the edges.

Most specimens from bomb No. 1 and bomb No. 7 were found in the bay; scattering was restricted to short distances. Stainless steel Type 410 specimens (AA, Figure 17) exhibited low temperature brittle fracture (by impact), which indicates that the specimen was cold when failure of the bomb occurred. Tantalum specimens (AA) in the gas phase exhibited excessive

distortion and edge burning, but those in the liquid phase were not severely distorted. Titanium All0AT specimens exhibited sustained burning, particularly in the gas phase (T, Figure 18).

#### 4.3 Teflon Racks

The test specimens were press-fitted into V-grooves 1/4 in. apart in Teflon rack assemblies (Figure 19) for support in the stainless steel bombs. The racks were machined from LOX grade Teflon TFE. Approximately 300 g of this material was present in each bomb. Pieces of the racks were scattered over a wide area, in general in the northerly direction of the wind (see Figure 20). The pieces recovered almost completely account for the 15 racks used in the tests. Most of the pieces were filled with bubbles and blow holes which did not previously exist (see Figure 21).

Where the Teflon pieces fell on grass, fires were started. Where they fell on noncombustibles, a white deposit was found on the surface around the Teflon. One piece came to rest on the stem of a bimetallic dial thermometer, the needle of which was stuck at a temperature of 370°C. Some of the pieces (six in all) were found relatively intact, although most were broken up into small fragments. The lengths the pieces left intact ranged from 3 to 3-1/8 in., compared to the original length of 3-1/4 in. The width was 7/8 in., compared to the original 1 in. The thickness of the pieces, however, was slightly larger than the original 1/4 in. Weights of some of the porous pieces were up to 25% less than the weights of identically sized portions of virgin Teflon.

Attempts were made to evaluate composition changes of the Teflon pieces collected. Chemical analysis showed that the original material had 24.7%C and exposed pieces 24.5-25.4%. It was difficult to obtain reproducible fluorine analysis due to the high fluorine content of the specimens. Attempts were also made to determine if, during fabrication of this material, trace amounts of hydrogen were introduced. Analysis showed 0.4 to 0.6% hydrogen. Although a certain amount of moisture or HF could be picked up from the atmosphere after explosion, this amount is excessive and the virgin Teflon also had 0.4% hydrogen.

From the condition of the Teflon pieces, it appears that this material was involved in a reaction with oxygen difluoride —  $(\text{CF}_2)_n + n\text{F}_2\text{O} \rightarrow n\text{CF}_4 + n/2 \text{O}_2$ . This reaction is exothermic and gives 4.6 Kcal. Furthermore,

even without heat evolution, the temperature of the bombs being above the critical temperature of oxygen ( $-119^{\circ}$ ), this reaction involves an abrupt increase in pressure.

#### 4.4 Oxygen Difluoride

The  $\text{OF}_2$  used in the tests was supplied by General Chemical, a division of Allied Chemical Corp. Analyses were received from the supplier with each cylinder of  $\text{OF}_2$ . These analyses are listed in Table III.

It will be noted that oxygen difluoride used in Test FO-17 was relatively pure compared to that used in Test FO-10, and that the  $\text{CO}_2$  and  $\text{CF}_4$  contents were comparatively small. A check analysis is underway and the results of tests have not yet been completed. The supplier does not run analyses of other impurities in  $\text{OF}_2$ . Samples have been taken and shipped to Dr. A. Salomon of Armour Research Foundation for chromatographic analysis of impurities. Results have not yet been received.

It should be pointed out that 3 lb of  $\text{OF}_2$  were shipped to Aerojet General Corp. as replacement of some oxidizer previously loaned to us. It was reported<sup>(5)</sup> that the stainless steel injector tube manifold (and one day later, the transfer line) of the rocket engine firing stand burned through and caused fire (in locations marked by arrows in Figure 22) while using the oxidizer received from cylinder R-4145.

It appears that oxygen difluoride used in Test FO-17 (which was the source of the initial explosion) was more reactive than that used in Test FO-10.

#### 4.5 Possible Mechanism of Explosion

From the observations reported above, it may be concluded that an intense and rapid chemical reaction, or thermal or adiabatic decomposition, took place in each of the test bombs, leading to a deflagrating explosion. The total energy evolved from the reaction or decomposition varied considerably from bomb to bomb, as evidenced by scattering of the bomb contents and the severity of erosion in the area of the gasket sealing surfaces, the latter caused by the outrush of gases, apparently at sonic flow rates (in the range of mach 1 to 1.5).

The generation of gaseous products and the explosive decomposition of  $\text{OF}_2$  or its reaction products created sufficiently large pressures to cause tensile impact failure of all six bolts holding the lids in place in each bomb, and blew out some of the lids through the roof to a considerable distance from the test bay. It was estimated that approximately 6000 psi gas pressure is required to tensile-break the bolts under static loading, and perhaps 3000-4000 psi under dynamic tensile loading. The magnitude of the pressures developed in the bombs was certainly considerably higher than these figures.

One of the bombs in Test FO-17 was the source of the initial explosive reaction. The distinct imprint of the base of one bomb on the bottom of the jacket of the insulated bath is direct evidence of this occurrence. The initial deflagration or detonative reaction apparently occurred when the technician was gently tamping Dry Ice into place with a wooden stick. The total energy produced by this tamping operation in general is not greater than 2 in.-lb. Propagation of pressure waves between the bombs in Test FO-17, and between Tests FO-17 and FO-10, of course was sufficiently high to initiate sympathetic explosion in other bombs.

It should be noted that tests PNF-10 and PNF-13 were also in the test bay, and the test bombs received very large shock pressure waves, as evidenced by twisting of the support rods holding the bombs in place and by damage to the insulating bath surrounding the bombs. Nonetheless, they did not explode. These tests contained a mixture of 50% perchlorylfluoride ( $\text{FClO}_3$ )-50% tetrafluorohydrazine ( $\text{N}_2\text{F}_4$ ) at  $-109^\circ\text{F}$  and low pressure (about 15 psi).

The test bombs which exhibited deflagration or detonative reactions were all processed similarly, although they contained somewhat different test specimens. Apparently one of the bombs in Test FO-17 had some component or reaction product more sensitive to shock which served as the source of the initial explosion. This bomb was not positively identified, but indications are that it was bomb No. 13, which exhibited a wide scattering pattern and contained a number of test materials which showed reactive characteristics (graphite, Ti alloy All0-AT, columbium, tantalum, etc.).

Since all test bombs containing  $\text{OF}_2$  exhibited deflagration or detonative reactions, the components in these tests which appear to be suspect as to

shock sensitivity to  $\text{OF}_2$  reactions are of great importance in determining mechanism of explosion. Following is a summary of such suspect components.

- (1) Test material which exhibited reactive tendencies
  - a. Graphite, AGKSP grade, with impurity constituents such as Al, Cu, Fe, Mg, Si, etc., each less than 1 ppm
  - b. Titanium Al10-AT containing Al 5.2, Sn 2.4, Fe 0.34, C 0.026,  $\text{N}_2$  0.028, and  $\text{H}_2$  0.015
  - c. Tantalum containing  $\text{O}_2$  50 ppm,  $\text{N}_2$  30 ppm, C 20 ppm, W 50 ppm, Cb 10 ppm, and Fe 8 ppm
  - d. Columbium containing Cb 99.70,  $\text{O}_2$  0.03,  $\text{N}_2$  0.03, C 0.01, and Ta 0.05
  - e. Teflon FEP copolymer of tetrafluoroethylene and hexafluoropropylene
- (2) Support racks
  - a. Teflon TFE polymer of tetrafluoroethylene
- (3) Residues deposited on the bomb
  - a. Oily residues previously found in test bombs in trace quantities
  - b. Sample residues that gradually dissolve in  $\text{OF}_2$
- (4) Impurities of  $\text{OF}_2$

It should be pointed out that in studying the impact sensitivity of materials with  $\text{OF}_2$ , the role of impurities (particular H, C, and N in specimens such as Ti, Ta, Cb, steels, etc.) in dissolving or gradually diffusing to the surface and reacting with  $\text{OF}_2$  is not known.

In several previously completed tests using  $\text{N}_2\text{F}_4$ - $\text{FClO}_3$  blend, and in one test using  $\text{OF}_2$ , trace quantities of oily residues were found in the test bomb after removal of specimens at the end of the tests. Infrared analysis seems to indicate that these residues contain Kel-F grease and traces of hydrocarbons (C-H and C=O or HC=O bonds).

The shock sensitivity of these various suspect materials with  $\text{OF}_2$ , and the shock sensitivity of  $\text{OF}_2$  itself at various impurity contents and under high pressures, are not known and require thorough investigation to determine the true mechanism of the accidental explosion reported here.

TABLE I  
TEST FO-17 CONDITIONS AND MATERIALS

Test Conditions

Temperature: -109°F  
Pressure before explosion: 505 psi  
Design duration: 4 months  
Actual duration: 7 days

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
<u>I. Specimen from Bomb No. 5</u>			
Al Alloy 1100-0	0.040	D.2.A D.11.A	Gas
Al Alloy 2014-T6	0.040	H.7.B H.9.B	Gas
Al Alloy 2219-T6	0.048	D.4.D D.5.D	Gas
Al Alloy 5456-T6	0.040	A.14.E F.5.E	Gas
Al Alloy 6061-T6	0.040	A.6.F D.4.F	Gas
Al Alloy 7079-T6	0.048	C.4.H C.8.H	Gas
Teflon FEP	0.030	AC.12	Gas
<u>II. Specimens from Bomb No. 8</u>			
SS 301 FH	0.025	G.4.1	Gas
		H.4.1	
		H.5.1	Liquid
		H.6.1	
SS 316 A	0.025	J.9.J	Gas
		K.5.J	
		J.10.J K.6.J	Liquid
SS 316 FH	0.025	P.3.AO	Gas
		R.1.AO	
		E.1.AO O.2.AO	Liquid



TABLE I (CONT'D)  
TEST FO-17 CONDITIONS AND MATERIALS

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
SS 347 A	0.025	F.6.K	Gas
		F.7.K	
		E.2.K	Liquid
		E.6.K	
SS 347 FH	0.025	K.1.AP	Gas
		T.1.AP	
		A.1.AP	Liquid
		Q.3.AP	
SS 410 UTS200	0.025	M.2.L	Gas
		M.7.L	
		L.6.L	Liquid
		M.4.L	
PH-15-7 Mo-RH1050	0.025	M.8.M	Gas
		M.9.M	
		L.3.M	Liquid
		M.5.M	
AM-350 CRT	0.025	G.1.N	Gas
		G.4.N	
		H.5.N	Liquid
		H.9.N	
III. <u>Specimens from Bomb No. 13</u>			
Nickel 200 A	0.025	G.3.P	Gas
		G.9.P	
		G.4.P	Liquid
		G.8.P	
Inconel X-UTS150	0.025	G.2.R	Gas
		G.4.R	
		G.3.R	Liquid
		G.5.R	
Rene' 41-UTS180	0.025	H.2.S	Gas
		H.8.S	
		H.7.S	Liquid
		H.10.S	

TABLE I (CONT'D)  
TEST FO-17 CONDITIONS AND MATERIALS

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
Ti Alloy Al10-AT-A	0.025	J. 10. T	Gas
		K. 3. T	
		J. 3. T	Liquid
		K. 7. T	
Columbium A	0.010	U. 2. Y	Gas
		Y. 2. Y	
Tantalum A	0.010	A. 2. AA	Gas
		U. 2. AA	
		S. 2. AA	Liquid
		T. 2. AA	
Cufenloy 40-A	0.040	V. 1. AK	Gas
		V. 3. AK	
		U. 1. AK	Liquid
		U. 3. AK	
Cufenloy 10-A	0.040	60. AQ	Gas
		64. AQ	
		52. AQ	Liquid
		54. AQ	
Graphite AGKSP	0.25 dia rod	S. 40. AH	Gas
		L. 41. AH	
		S. 42. AH	Liquid
		L. 43. AH	

TABLE II  
TEST FO-10 CONDITIONS AND MATERIALS

Test Conditions

Temperature:	-109°F
Pressure before explosion:	503 psi
Design duration:	12 months
Actual duration:	6 months
Initial oxidizer loading:	25 Apr 1963
Second oxidizer loading:	11 Sept 1963
Explosion:	15 Oct 1963

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
I. <u>Specimens from Bomb #3</u>			
Al Alloy 1100-0	0.040	F.2.A	Gas
		F.11.A	
		D.10.A	Liquid
		J.4.A	
Al Alloy 2014-T6	0.040	C.11.B	Gas
		F.3.B	
		F.14.B	Liquid
		H.4.B	
Al Alloy 2219-T6	0.040	E.3.D	Gas
		E.14.D	
		G.1.D	Liquid
		G.7.D	
Al Alloy 6061-T6	0.040	A.5.F	Gas
		H.13.F	
		E.11.F	Liquid
		E.12.F	
Al Alloy 7079-T6	0.048	B.5.H	Gas
		B.8.H	
		B.12.H	Liquid
		G.6.H	

TABLE II (CONT'D)  
TEST FO-10 CONDITIONS AND MATERIALS

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
Columbium A	0.010	S. 1. Y Z. 3. Y	Gas
		R. 1. Y W. 1. Y	Liquid
Teflon FEP	0.030	AC. 18 AC. 19	Gas
		AC. 25 AC. 27	Liquid
II. <u>Specimens from Bomb #1</u>			
SS 301 FH	0.025	F. 7. 1 L. 4. 1	Gas
		J. 7. 1 L. 7. 1	Liquid
SS 316 A	0.025	F. 3. J	Gas
		A. 10. J A. 11. J	Liquid
SS 316 FH	0.025	A. 1. AO B. 1. AO	Gas
		A. 3. AO C. 2. AO	Liquid
S 347 A	0.025	E. 9. K	Gas
		C. 2. K A. 11. K	Liquid
SS 347 FH	0.025	F. 1. AP	Gas
SS 410-UTS200	0.025	L. 4. L	Gas
		F. 3. L E. 7. L	Liquid

TABLE II (CONT'D)  
TEST FO-10 CONDITIONS AND MATERIALS

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
PH 15-7 Mo-RH 1050	0.025	F. 7. M F. 11. M	Liquid
AM-350 CRT	0.025	F. 1. N F. 11. N	Gas
		E. 4. N E. 7. N	Liquid
Tantalum A	0.010	Y. 1. AA	Gas
		H. 1. AA M. 3. AA	Liquid
III. <u>Specimens from Bomb #7</u>			
Nickel 200 A	0.025	A. 10. P A. 11. P	Gas
		B. 10. P C. 2. P	Liquid
Inconel X-UTS 150	0.025	G. 6. R G. 8. R	Gas
		E. 9. R F. 4. R	Liquid
Rene' 41-UTS 180	0.025	E. 5. S F. 9. S	Gas
		E. 7. S F. 8. S	Liquid
Cufenloy 40-A	0.040	U. 3. AK V. 2. AK	Gas
		F. 3. AK G. 3. AK	Liquid
Electroless Nickel Plate on Cufenloy 40	0.040	L. 1. AN L. 3. AN	Liquid

TABLE II (CONT'D)  
TEST FO-10 CONDITIONS AND MATERIALS

<u>Material</u>	<u>Specimen Thickness</u>	<u>Specimen Code</u>	<u>Phase</u>
Cufenloy 10-A	0.040	12.AQ	Gas
		25.AQ	
		5.AQ	Liquid
		7.AQ	
Copper A	0.037	G.11.V	Liquid
Ti Alloy A110-AT-A	0.025	J.1.T	Gas
		J.8.T	
		B.7.T	Liquid
		B.9.T	

TABLE III

ANALYSIS OF OXYGEN DIFLUORIDE  
AS SUPPLIED BY ALLIED CHEMICAL CORP.

<u>Test</u>	<u>Cylinder No.</u>	<u>OF<sub>2</sub>, %</u>	<u>O<sub>2</sub>, %</u>	<u>CO<sub>2</sub>, %</u>	<u>CF<sub>4</sub>, ppm</u>
FO-10	230-4658	97.02	2.48	0.35	1500
	230-3444	97.04	2.28	0.43	2100
	R-3489	98.40	0.80	0.33	1500
FO-17	R-4145	98.44	1.40	0.13	289

The oxygen difluoride used for Test FO-10 was loaned to Astropower by Aerojet General Corp. and represents the composition of the oxidizer present in the test when explosion occurred.

## 5.0 SUGGESTED HANDLING TECHNIQUES TO MINIMIZE POTENTIAL HAZARDS

Previous observations<sup>(2)</sup> had shown that Kel-F rubber was unstable in the presence of fluorinating agents. During the test program it was observed that Teflon and graphite absorbed the fluorinated oxidizers, but vacuum heating (120°C) removed the absorbate. Graphite had been immersed in gaseous  $\text{OF}_2$  for 21 days without any problems arising. The burning of titanium, columbium, and tantalum specimens showed that they are a potential hazard, but the conditions at which this reaction is initiated and the role of impurities are unknown.

It is recommended that carbon and carbon compounds, even perfluorinated ones, be kept from contact with  $\text{OF}_2$  unless further studies, such as impact tests, demonstrate that particular systems are safe. It is further recommended that a program of impact stability and shock sensitivity studies under both high and low pressures be initiated to test the hazards involved with various materials such as fluoropolymers, graphite, titanium, tantalum, columbium, magnesium, etc., in the presence of  $\text{OF}_2$ . Such studies should precede corrosion studies with all powerful oxidizing and reducing agents.

The use of remote handling and servicing devices should be mandatory wherever more than gram quantities of oxygen fluoride are used in systems which have not been positively proved to be safe.

The modification of the test apparatus for long-term immersion tests and for stress corrosion tests with  $\text{OF}_2$  and  $\text{N}_2\text{F}_4$ - $\text{FClO}_3$  blend, and also the generation procedure used for carrying out experiments involving  $\text{O}_3\text{F}_2$ - $\text{LO}_2$ , are being worked out to complete the program on compatibility of structural materials with high performance O-F liquid oxidizers under Contract AF33(657)-9162.



## REFERENCES

1. N. V. Sidgwick, Chemical Elements and Their Compounds, Vol. II, Clarendon Press, Oxford (1950) p 1136.
2. N. A. Tiner, W. D. English, and S. W. Pohl, "Compatibility of Structural Materials with High Performance O-F Liquid Oxidizers," Contract AF33 (657)-9162, Progress Reports 112-Q1, 112-Q2, 112-Q3, 112-Q4, and 112-Q5 (1962 and 1963).
3. Ellis R. Stout, Atomic Energy Commission TID-11461 (1961).
4. R. Pickford, "Design of Uncooled Flame Deflectors," ARS 582-58 (1958).
5. D. Smith, G. Shaffer and K. Kahn, Aerojet General Corp., private communication, (4 Nov 1963).

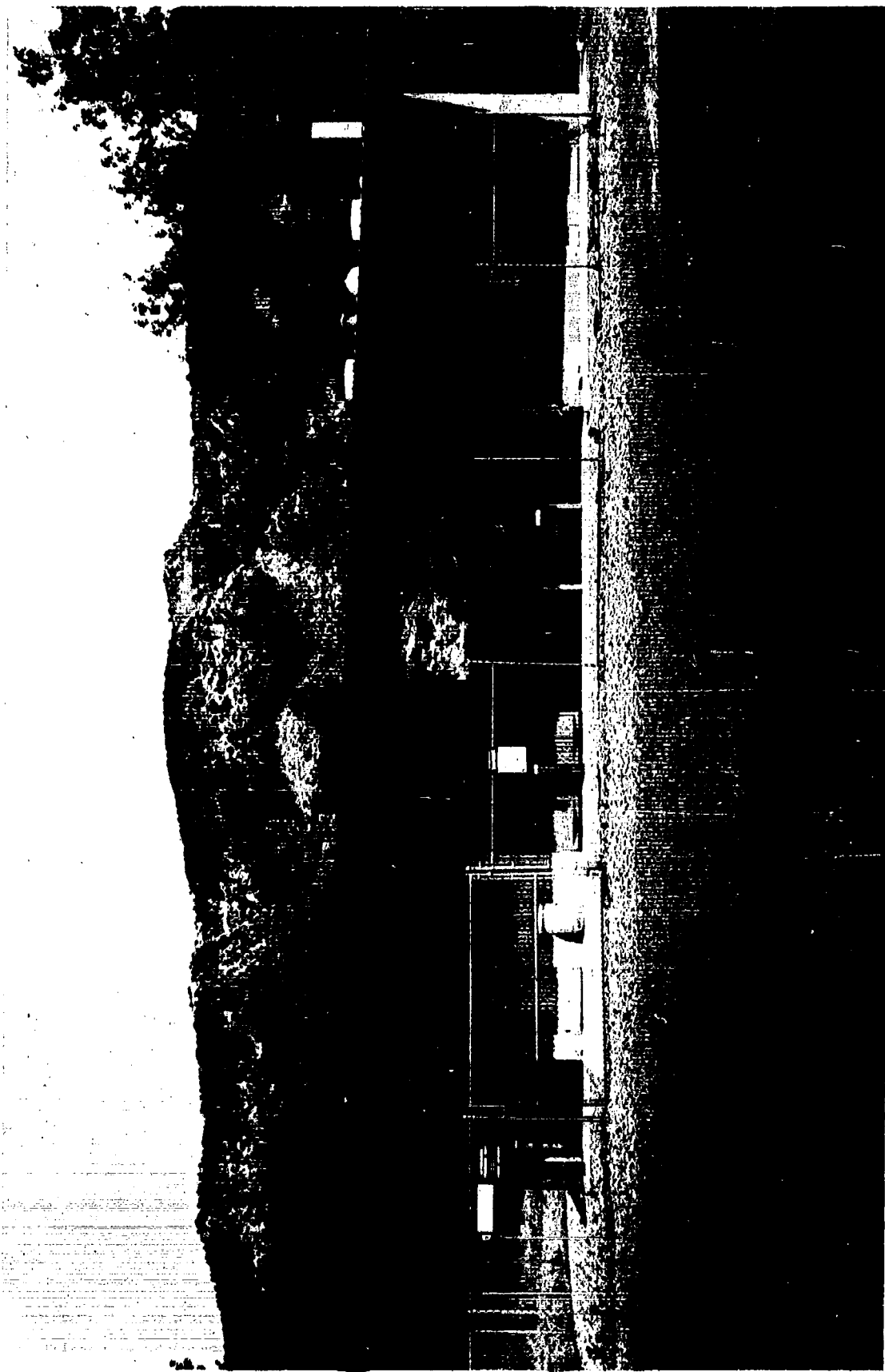


Figure 1. Fluorine Chemistry Facility, Gypsum Canyon Test Range  
(Physical Chemistry Laboratory on Right)



Figure 2. Long-Term Test Assembly Showing Five Tests in Progress

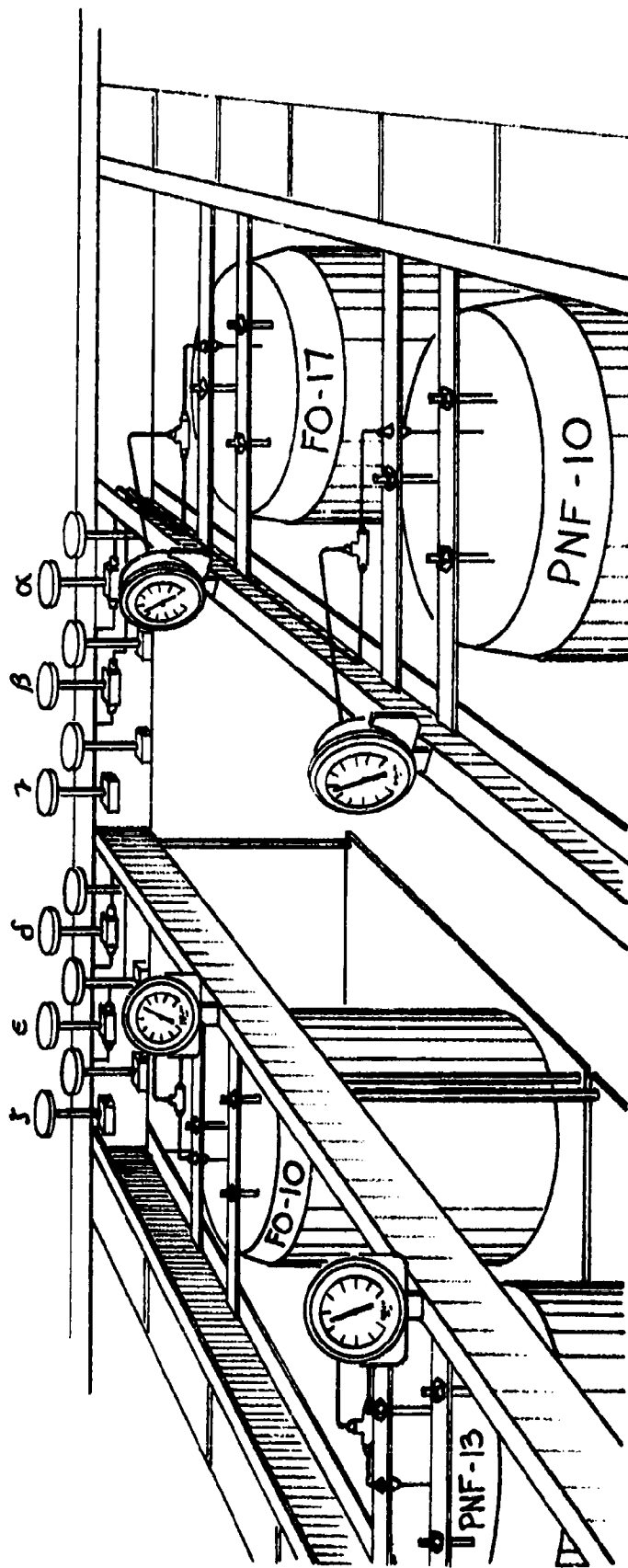
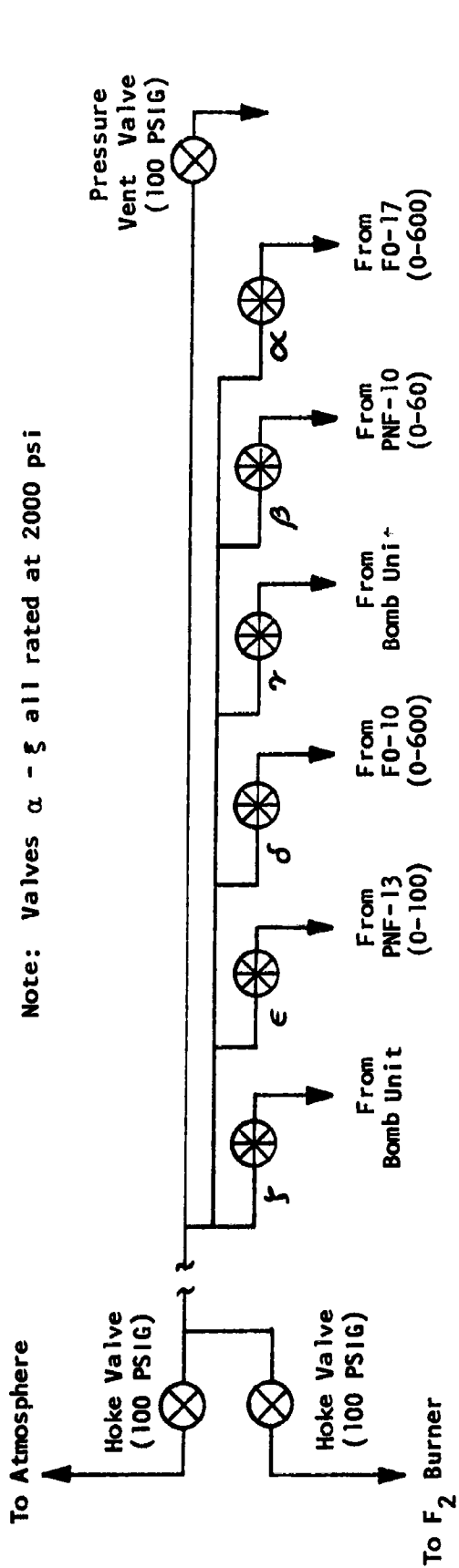


Figure 3. Top View of Long-Term Exposure Test Cells Illustrating the Position of the Test Bombs and Flow System

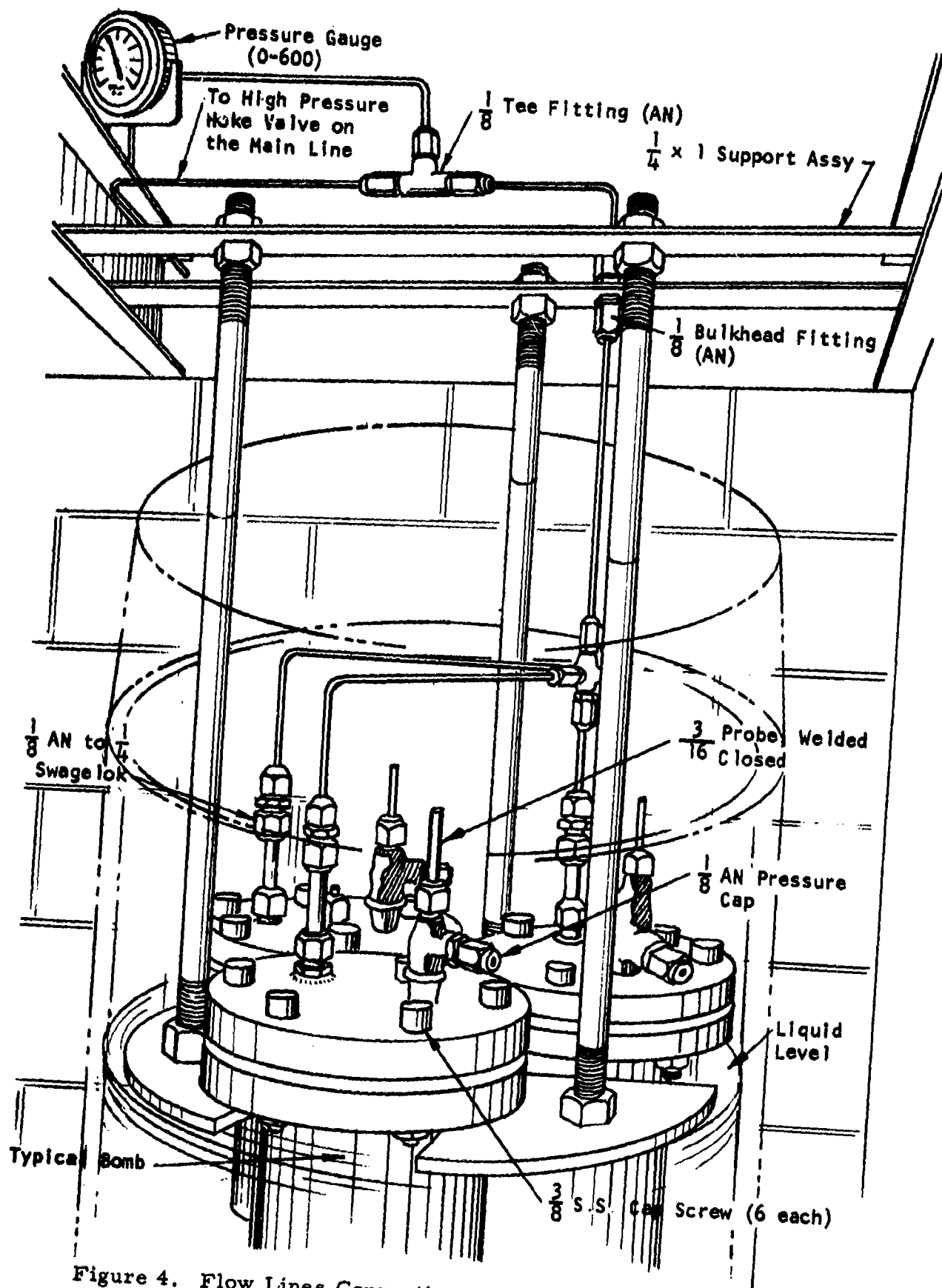


Figure 4. Flow Lines Connecting Test Bombs to Main Line

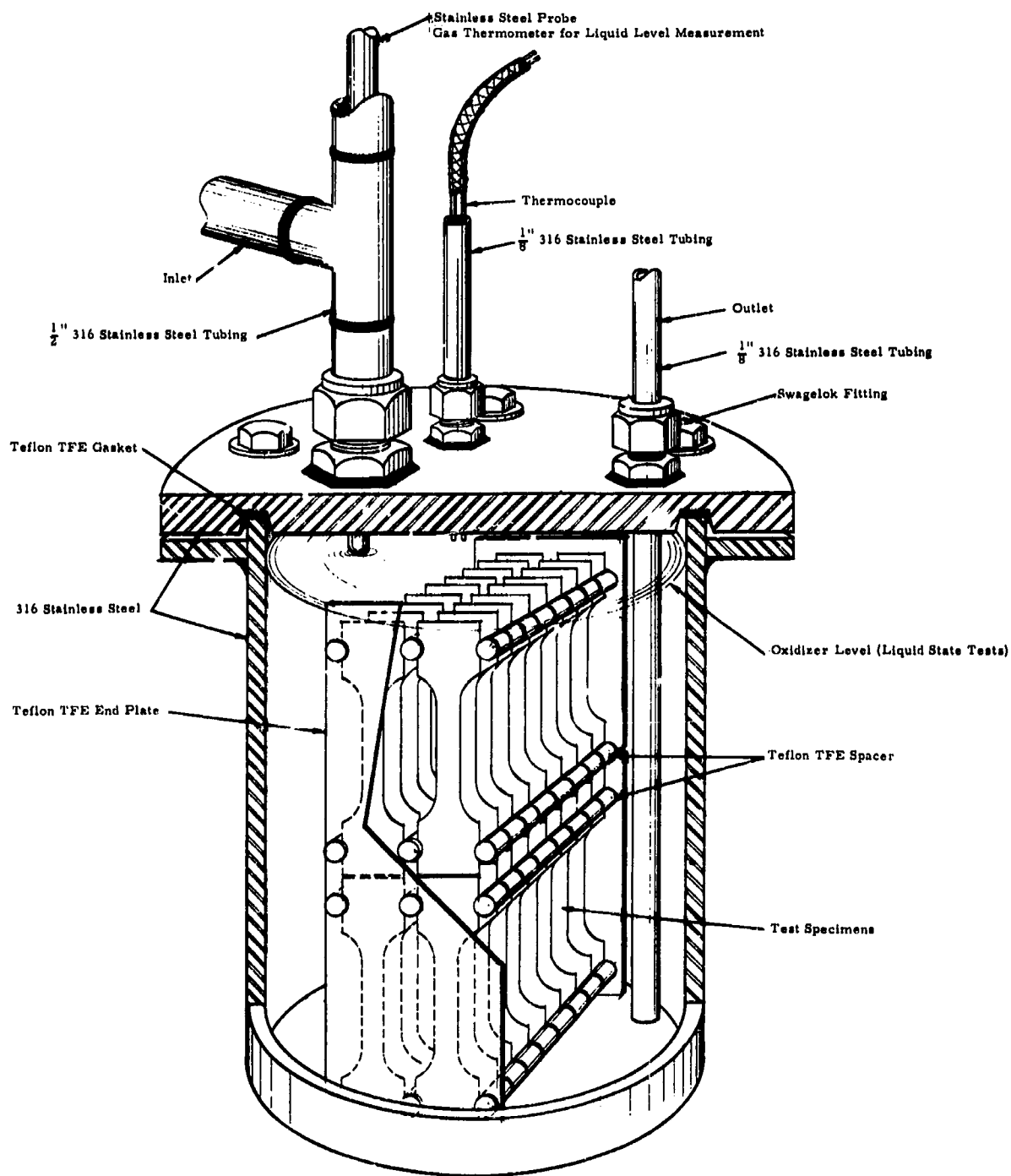


Figure 5. Cutaway Drawing of Sample Test Holder

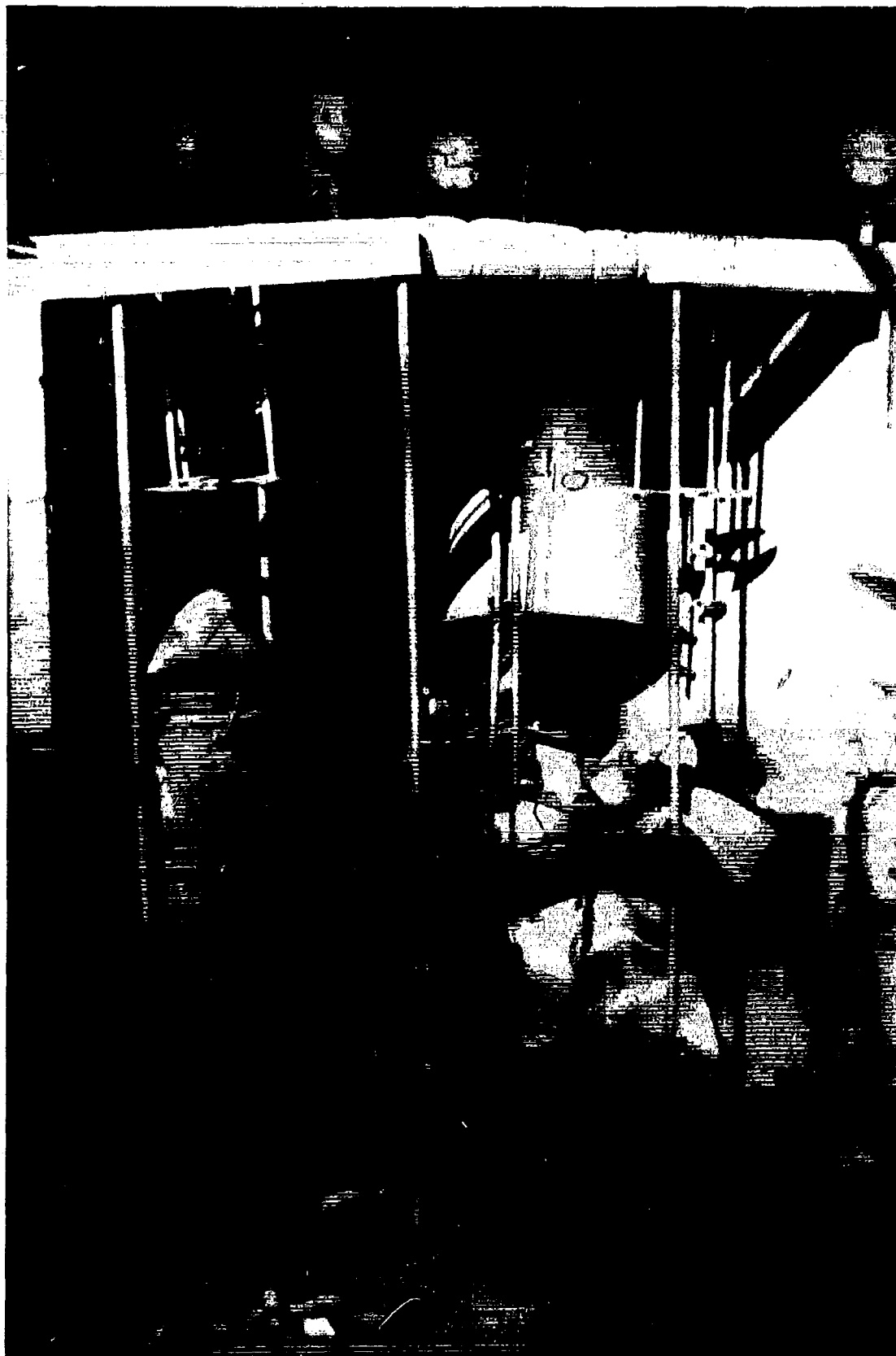


Figure 6. Long-Term Test Bay After Explosion

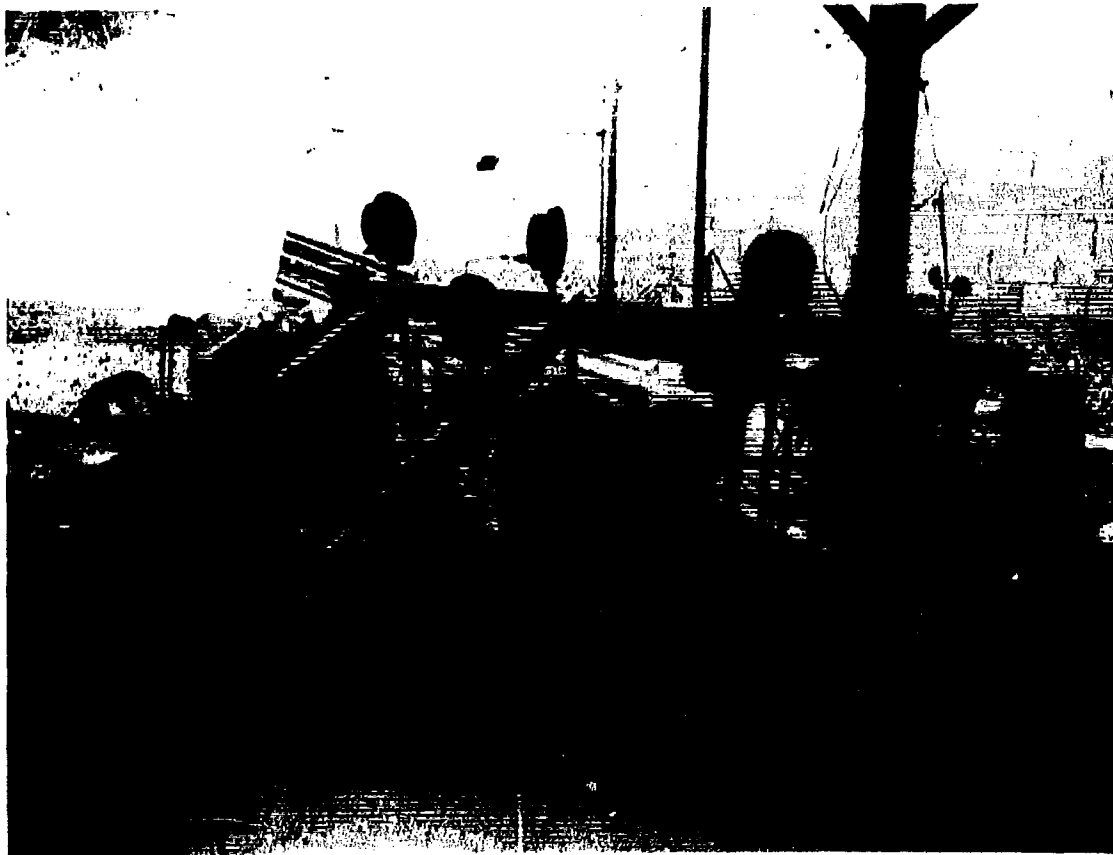


Figure 7. Top View of Long-Term Test Bay Showing Extent of Explosion Damage





Figure 8. Stainless Steel Tubing Showing "Banana Peel" Failure

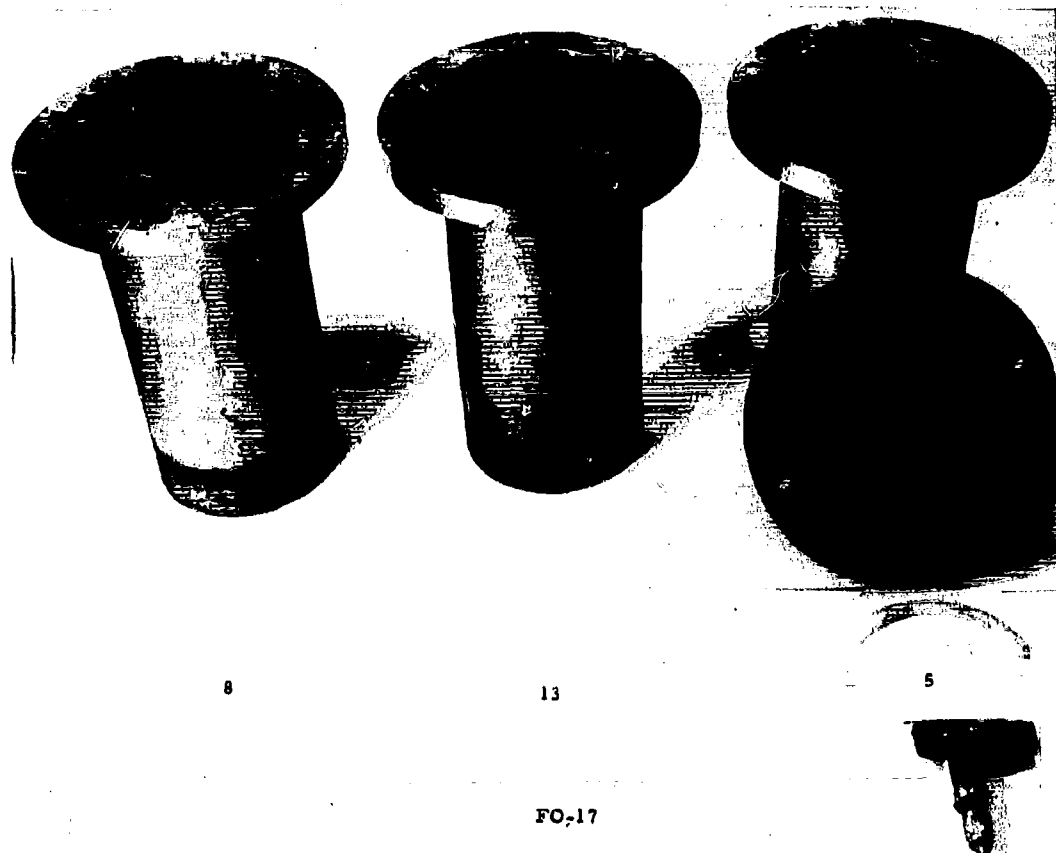
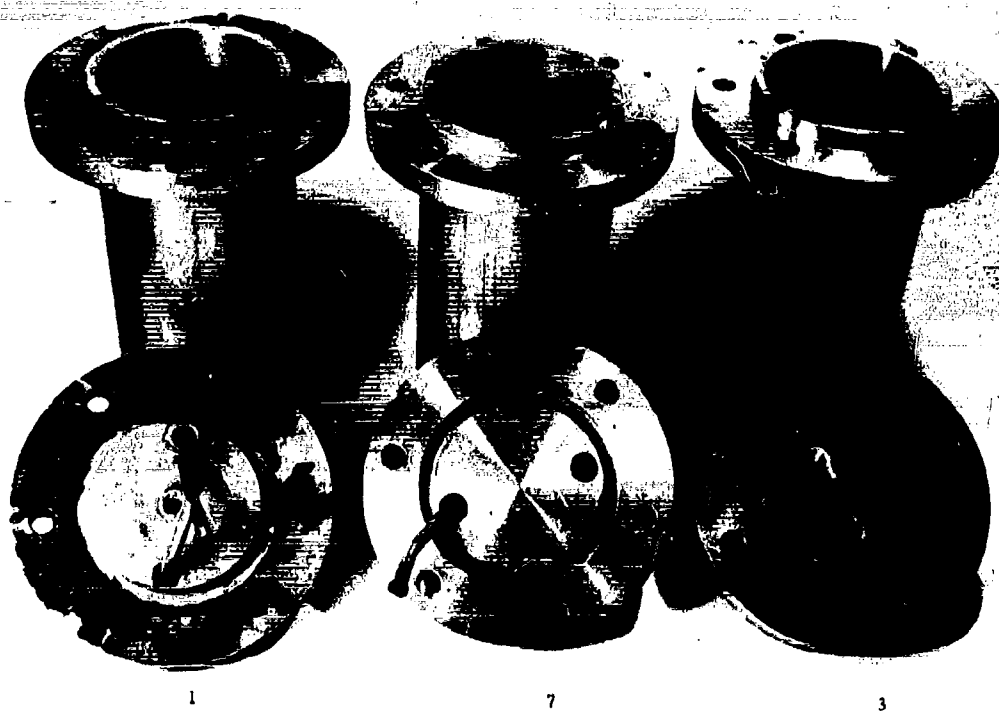


Figure 9. Photomacrograph Showing Appearance of Bombs from Test FO-17. Two of the lids were not found.



FO-10

Figure 10. Photomacrograph Showing Appearance of Bombs from Test FO-10

Legend

	In Bay 2	On Roof	% Scatter	% In Bay
$\triangle$ Bomb #5	1	1	91	10
$\square$ Bomb #8	10	2	69	31
$\circ$ Bomb #13	5	3	83	17

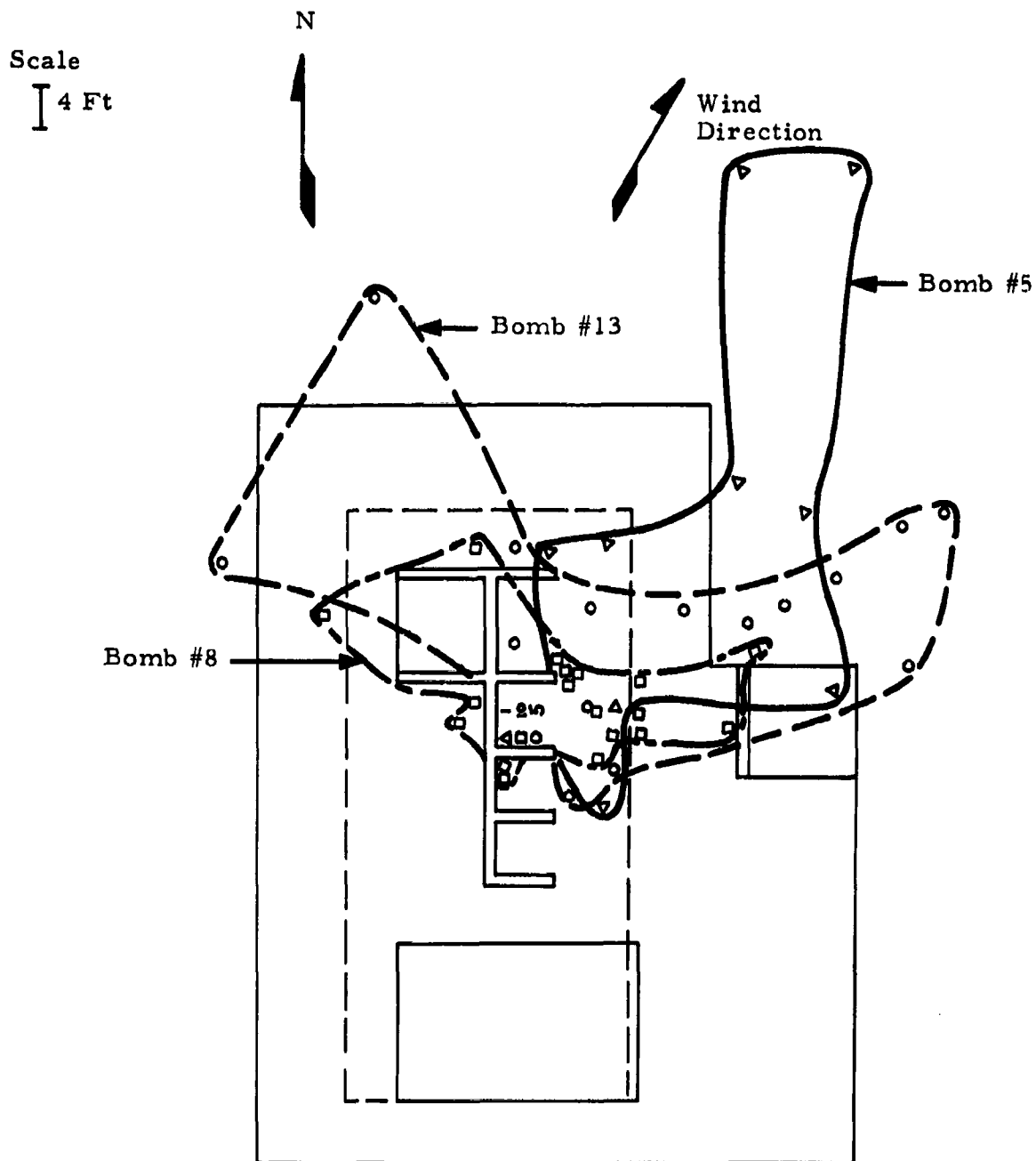


Figure 11. Scattering Pattern of Specimens from Test FO-17

# Legend

—○— Bomb #1

—△— Bomb #3

—□— Bomb #7

In Bay

On Roof

% Scatter

% In Bay

17

1

37

63

2

1

93

7

20

2

26

74

Scale

4 Ft

N

Wind  
Direction

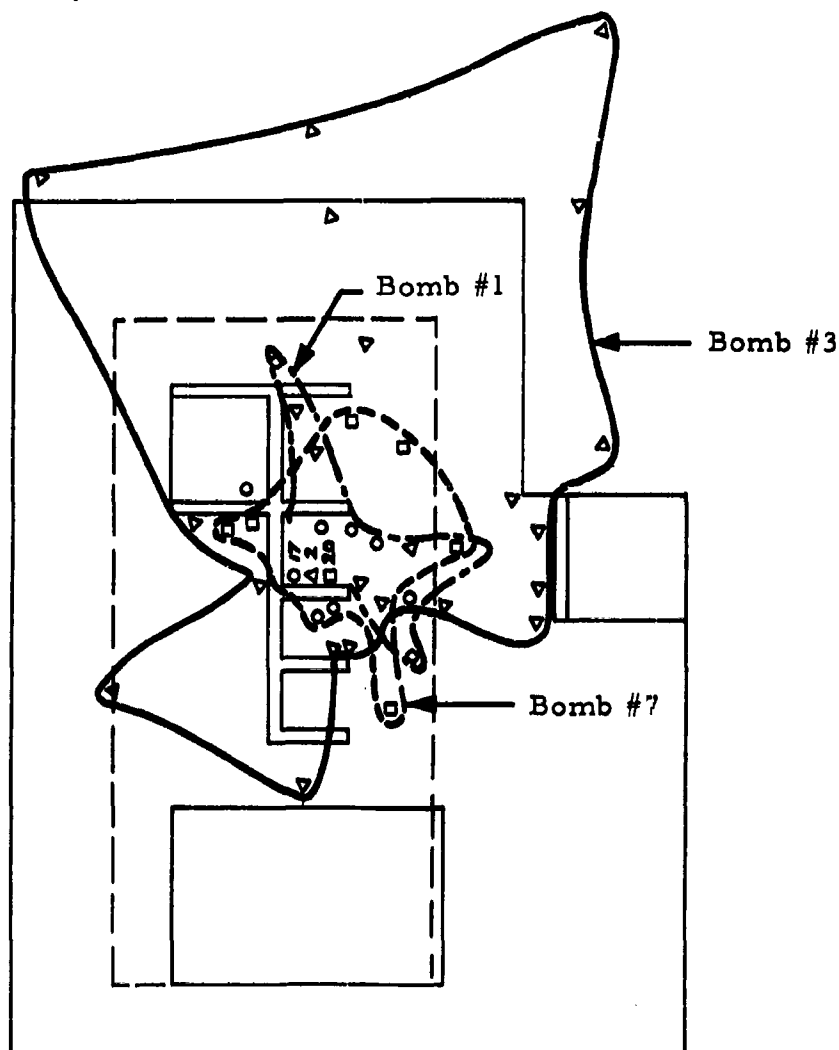
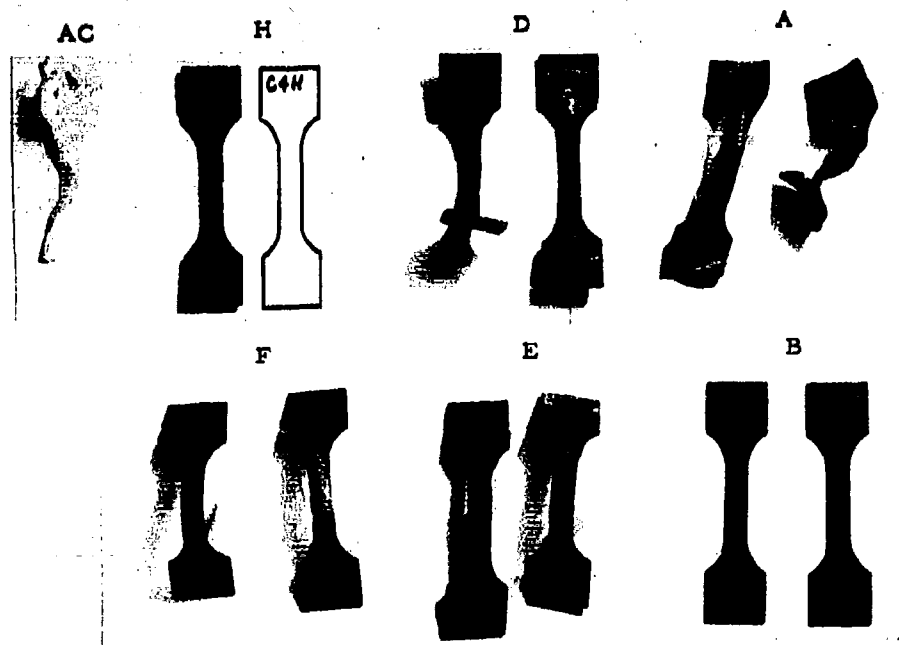


Figure 12. Scattering Pattern of Specimens from Test FO-10

**FO-17 BOMB 5**

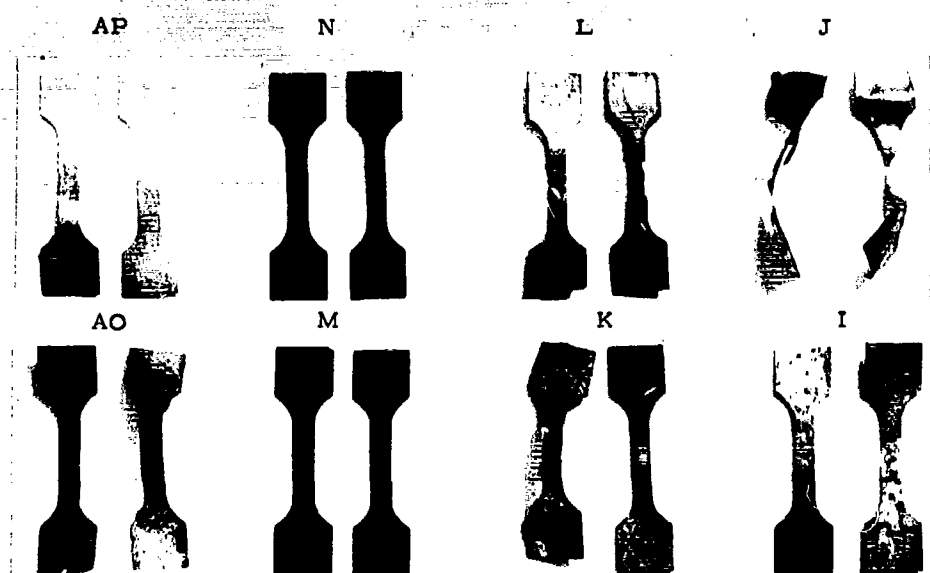
**ALL GAS PHASE**



**Figure 13. Appearance of Specimens from Bomb No. 5, Test FO-17.  
All Specimens immersed in gaseous phase.**

FO-17 BOMB 8

GAS



LIQUID

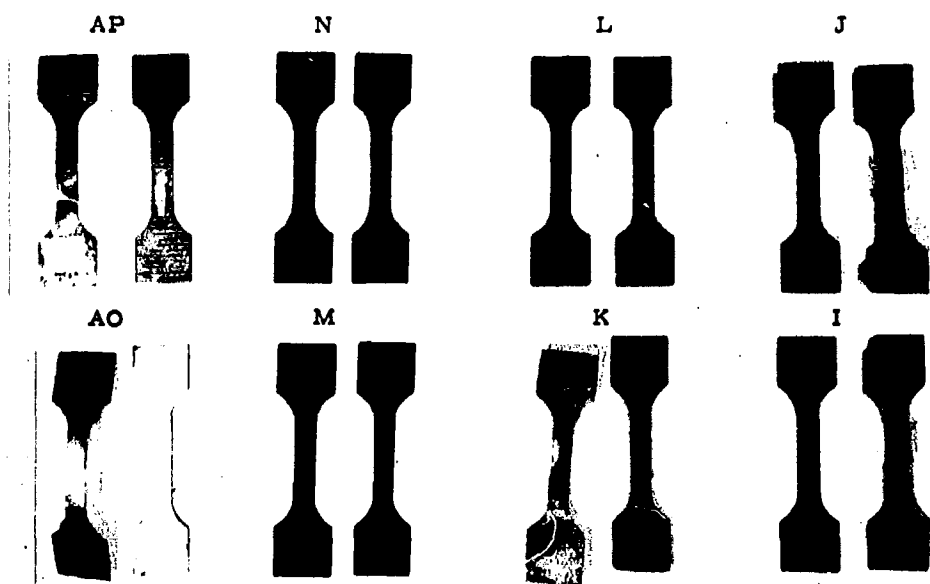
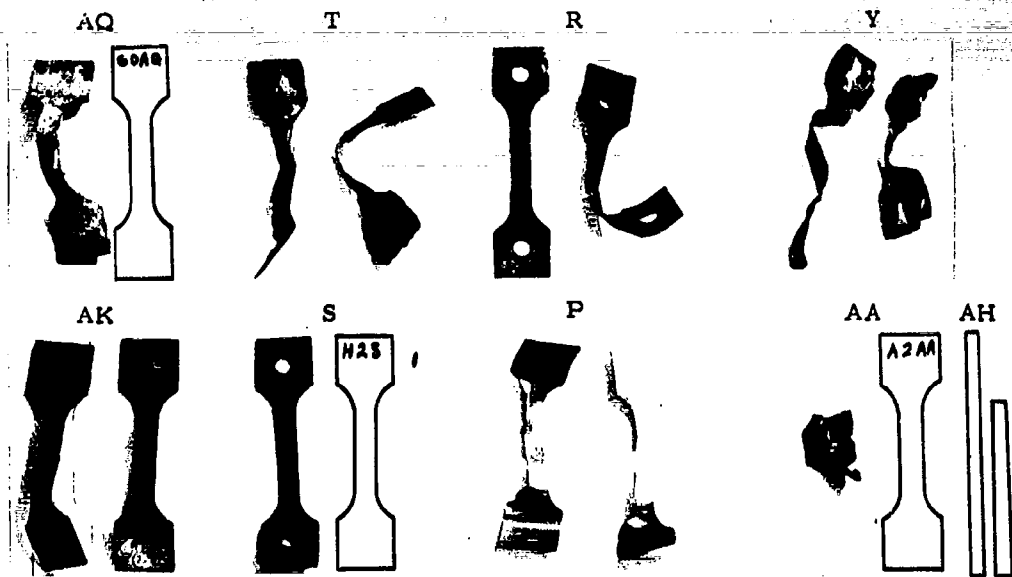


Figure 14. Appearance of Specimens from Bomb No. 8, Test FO-17

# FO-17 BOMB 13

## GAS



## LIQUID

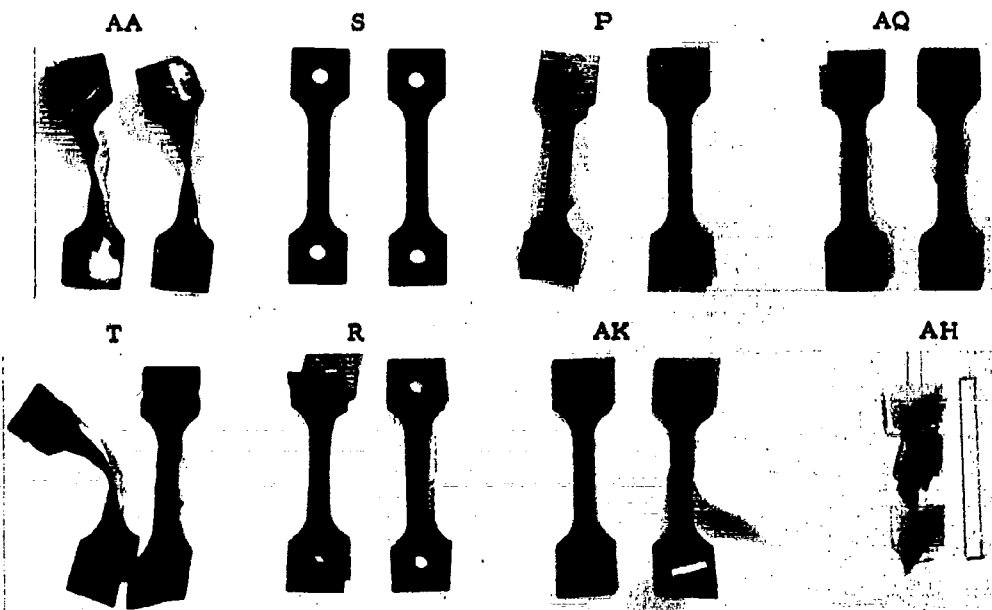
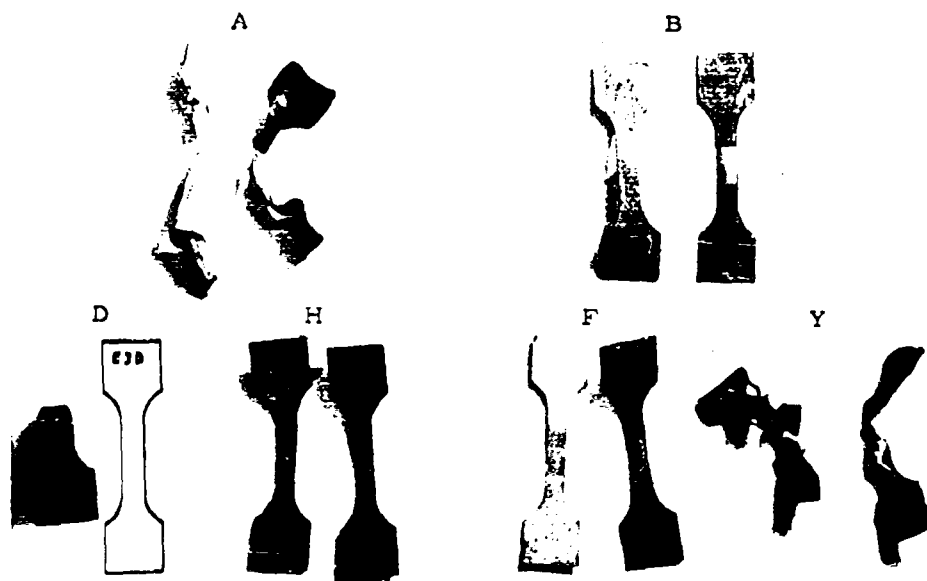


Figure 15. Appearance of Specimens from Bomb No. 13, Test FO-17



FO-10 BOMB 3

GAS



LIQUID

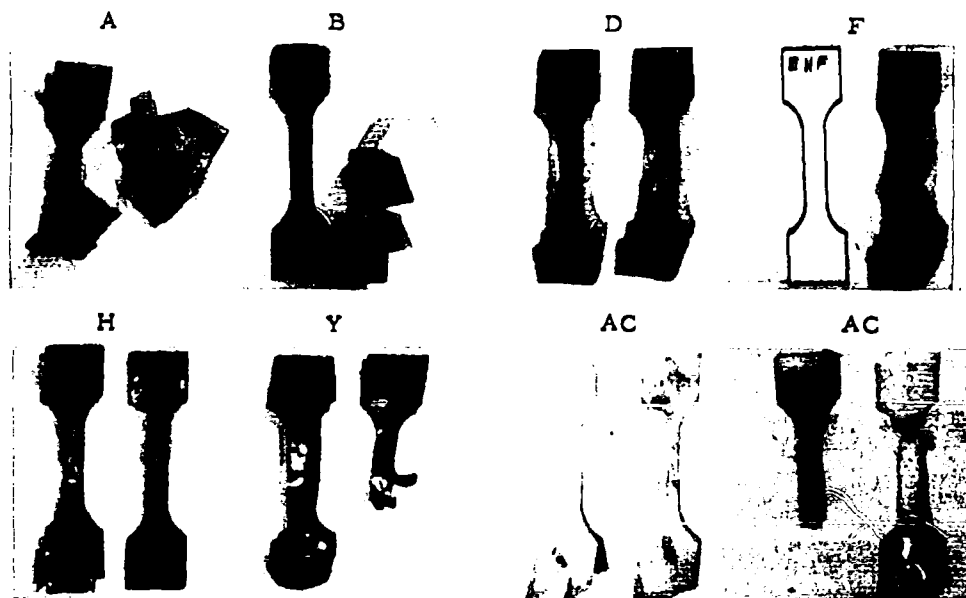
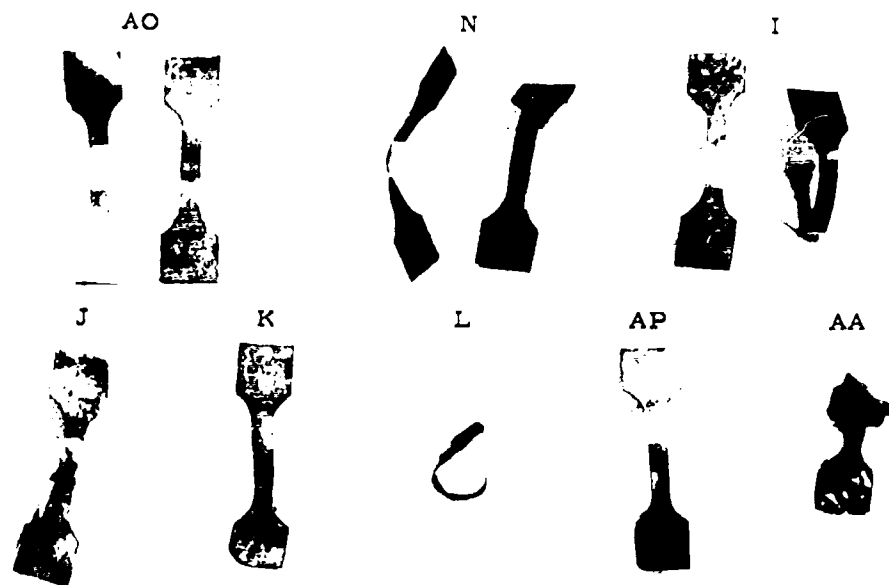


Figure 16. Appearance of Specimens from Bomb No. 3, Test FO-10

FO-10 BOMB 1

GAS



LIQUID

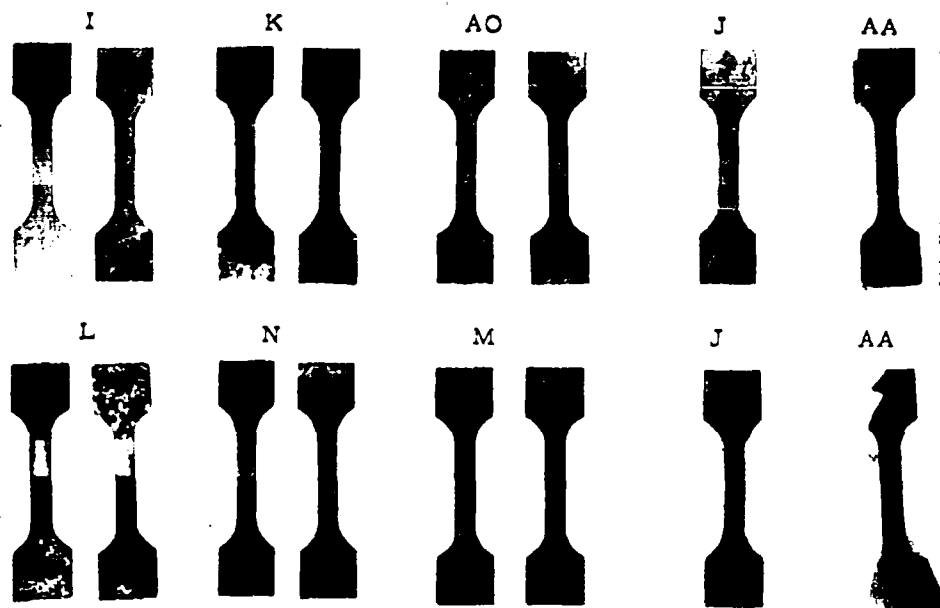
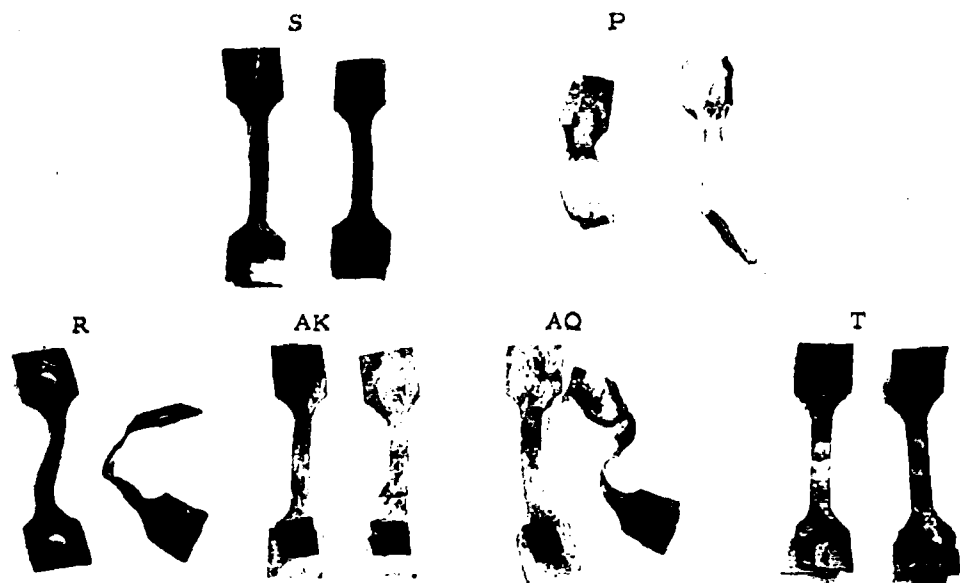


Figure 17. Appearance of Specimens from Bomb No. 1, Test FO-10

FO-10 BOMB 7

GAS



LIQUID

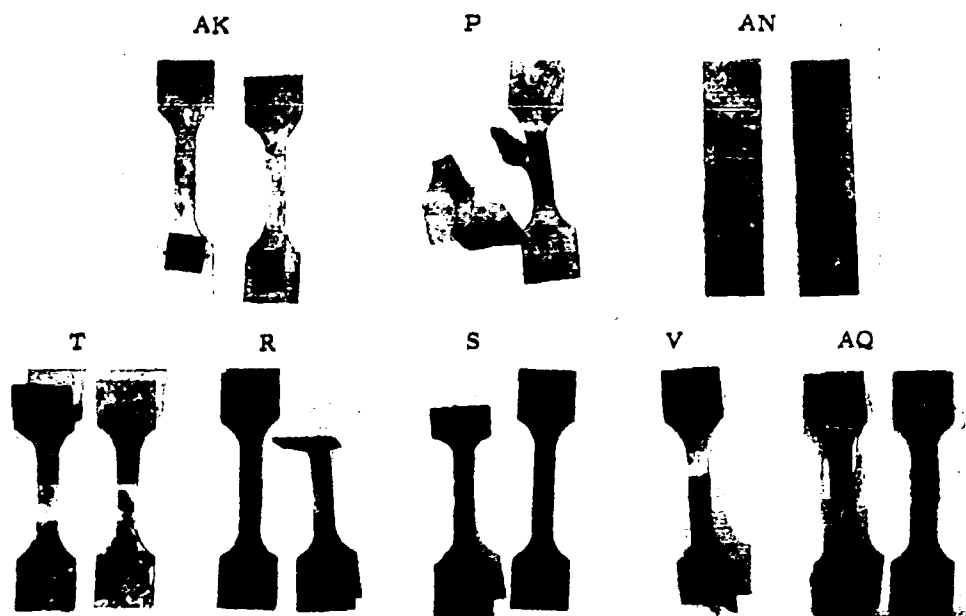


Figure 18. Appearance of Specimens from Bomb No. 7, Test FO-10

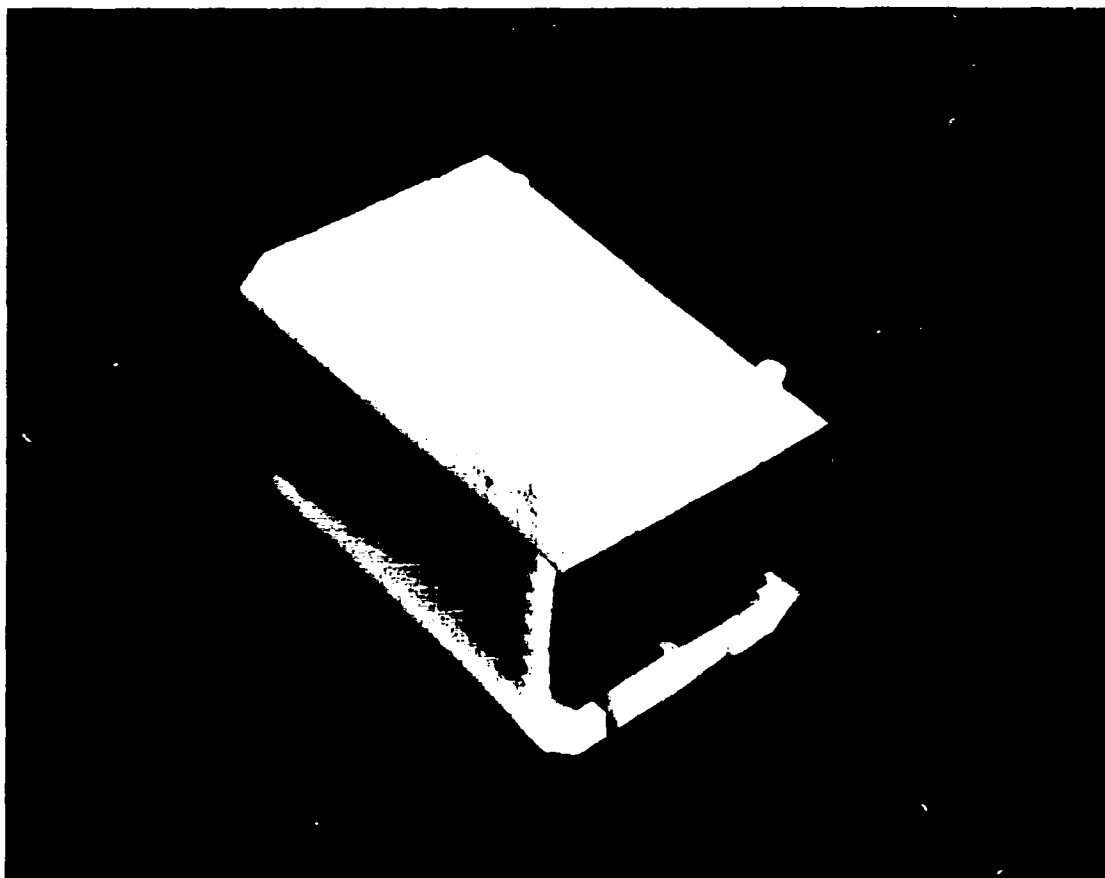


Figure 19. Teflon Rack Assembly Used to Support Test Specimens

Scale

I 4 Ft

N

Wind  
Direction

On Roof •  
On Ground ▼

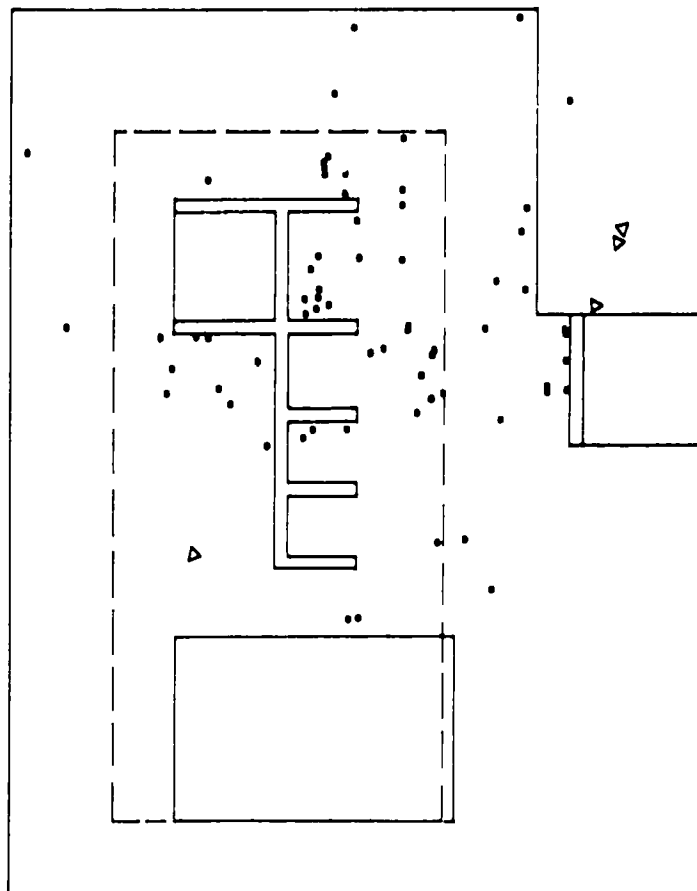
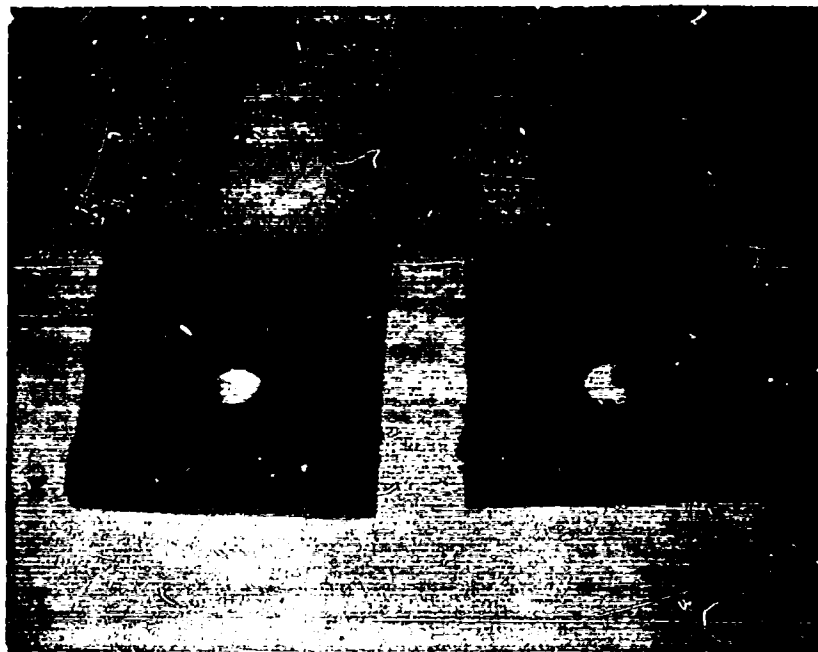


Figure 20. Scattering Pattern of the Pieces of Teflon Racks



a. As Collected



b. Section

Figure 21. Appearance of Teflon Pieces After Explosion

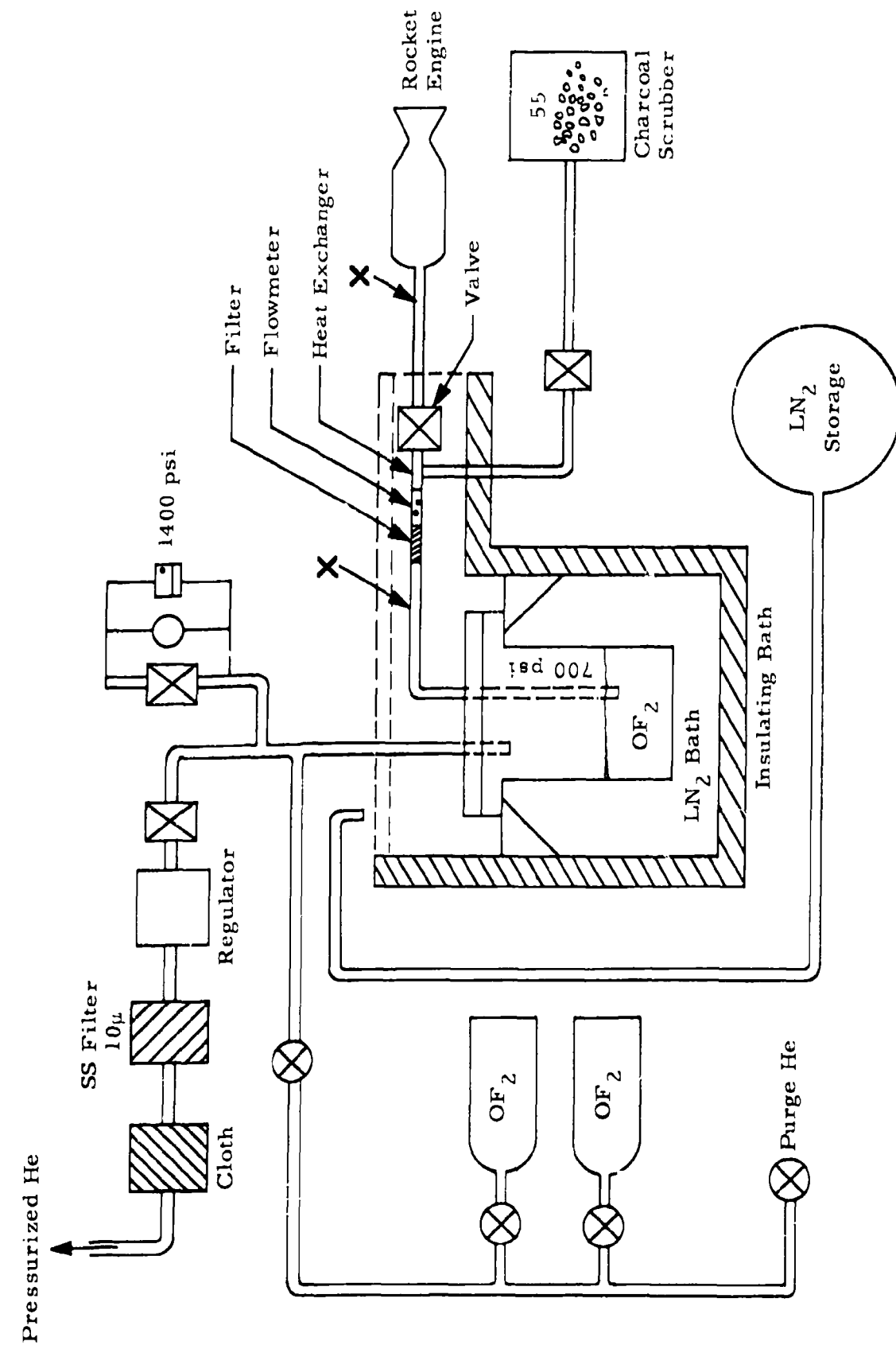


Figure 22. Simplified Schematic Diagram of Rocket Engine Firing Test Stand Illustrating Burning of Stainless Steel Tubing (Courtesy of Aerojet-General Corp.)